

# Flame Synthesis of Single-Walled Carbon Nanotubes and Nanofibers

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## Introduction

Carbon nanotubes are widely sought for a variety of applications including gas storage, intercalation media, catalyst support and composite reinforcing material [1]. Each of these applications will require large scale quantities of CNTs. A second consideration is that some of these applications may require redispersal of the collected CNTs and attachment to a support structure. If the CNTs could be synthesized directly upon the support to be used in the end application, a tremendous savings in post-synthesis processing could be realized. Therein we have pursued both aerosol and supported catalyst synthesis of CNTs. Given space limitations, only the aerosol portion of the work is outlined here though results from both thrusts will be presented during the talk.

Aerosol methods of SWNT, MWNT or nanofiber synthesis hold promise of large-scale production to supply the tonnage quantities these applications will require. Aerosol methods may potentially permit control of the catalyst particle size, offer continuous processing, provide highest product purity and most importantly, are scaleable. Only via economy of scale will the cost of CNTs be sufficient to realize the large-scale structural and power applications on both earth and in space.

Present aerosol methods for SWNT synthesis include laser ablation of composite metal-graphite targets or thermal decomposition/pyrolysis of a sublimed or vaporized organometallic [2]. Both approaches, conducted within a high temperature furnace, have produced single-walled nanotubes (SWNTs). The former method requires sophisticated hardware and is inherently limited by the energy deposition that can be realized using pulsed laser light. The latter method, using expensive organometallics is difficult to control for SWNT synthesis given a range of gas-particle mixing conditions along variable temperature gradients; multi-walled nanotubes (MWNTs) are a far more likely end products. Both approaches require large energy expenditures and produce CNTs at prohibitive costs, around \$500 per gram. Moreover these approaches do not possess demonstrated scalability.

In contrast to these approaches, flame synthesis can be a very energy efficient, low-cost process [3]; a portion of the fuel serves as the heating source while the remainder serves as reactant. Moreover, flame systems are geometrically versatile as illustrated by innumerable boiler and furnace designs. Addressing scalability, flame systems are commercially used for producing megatonnage quantities of carbon black [4]. Although it presents a complex chemically reacting flow, a flame also offers many variables for control, e.g. temperature, chemical environment and residence times [5]. Despite these advantages, there are challenges to scaling flame synthesis as well.

A 1g environment imposes a severe limitation on the timescale available for observing the catalyzed reaction. Buoyancy induced convection limits the entire time period for catalyst particle formation, CNT inception and growth to roughly 100 ms [6]. Therein the synthesis results may reflect kinetic constraints rather than fundamental reactivity differences based on thermodynamics. To achieve flow stability, a chimney or other flow guide is necessary in 1g. This imposes flow

restrictions, accentuates temperature gradients and generally restricts access to the reacting flow. With associated temperature gradients, non-laminar flow, nonuniform temperature and chemical species fields, basic knowledge of CNT inception periods, growth rates and deactivation processes remain unresolved.

Therein fundamental measurements are needed, unencumbered by buoyancy imposed limitations with uniform and well controlled environments of temperature, species concentrations and identities. With such foundational knowledge, practical large scale synthesis can be approached from a rational design perspective and not by Edisonian methods. With this ultimate goal, the objectives of the project of flame synthesis of carbon nanotubes were as follows:

1. To demonstrate flame synthesis of SWNTs and MWNTs.
2. Explore alternative methods of catalyst particle introduction into the flame environment.
3. Investigate the sensitivities to reactive gas environments, e.g. were PAHs involved (or even suitable) for CNT growth.

## Results and Discussion

### Onset of catalytic reactivity and selectivity based on gas identity

In our previous work pursuing a flame-aerosol approach, various methods of catalyst introduction have been studied; methods such as sublimation of organometallics [7-9], thermal evaporation of pure metals [10] or nebulization of solutions containing metal salts [11, 12] have been tested as a step towards scaling production. Initial work compared flame and high temperature furnace environments in order to identify optimum gas flows and an overall gas composition for SWNT synthesis [10]. Subsequent work made comparisons between two metals, Ni and Fe, and their catalyzed products, SWNTs and nanofibers, using a dual flame configuration [13, 14]. Recently LII has been applied to this system [15]. Using a variety of catalyst systems, we have consistently observed the following results. Fe reacted in both the CO and CO/C<sub>2</sub>H<sub>2</sub>-based gas mixtures, producing SWNTs. Fig. 1 shows TEM images of these products at various magnifications. In contrast, Ni was unreactive towards the CO gas mixture. It only reacted with the CO/C<sub>2</sub>H<sub>2</sub> gas mixture, producing nanofibers. This is shown in the TEM images of Fig. 2

### Ni

Further tests investigated in detail the size effects for Ni catalyst nanoparticles and sensitivities to the reactive gas mixture using the pyrolysis flame configuration. As with Fe, Ni nanoparticles were formed by thermal decomposition of a nebulized Ni nitrate solution entrained into a reactive fuel mixture. Although at the earliest stages of growth, the Ni nanoparticles were sufficiently small to catalyze single-wall nanotubes (SWNTs), only the larger particles appeared catalytically active yielding only nanofibers. Using different reactive gas mixtures consisting of CO or C<sub>2</sub>H<sub>2</sub> or their combination, Ni nanoparticles exhibited a high preferential reactivity towards C<sub>2</sub>H<sub>2</sub> to form nanofibers.

HRTEM images seen in Fig. 2 reveal that the carbon nanofibers consist of short, undulating carbon lamella forming the nanofiber walls. Where visible, the nanofiber tips are always terminated by a catalyst particle, in intimate association with the nanofiber walls. The structure of the fibers, relative size of the catalyst particles and contact of the carbon lamella with the particle are consistent with the traditional carbon fiber growth mechanism. Variation of the CO/C<sub>2</sub>H<sub>2</sub> ratio alters the nanofiber morphology rather little (though it is different with only C<sub>2</sub>H<sub>2</sub> present), instead the relative yield varies dramatically. Ni appears to be relatively unreactive towards CO within the flame environment used here for all particle sizes observed (0.5 - 5 nm). In contrast, Ni is catalytically active towards C<sub>2</sub>H<sub>2</sub>, but only the larger nanoparticles (4 - 5

nm) exhibit this activity. Both observations are attributed to the nanoparticle physical and electronic structure, and their variation with particle size, as later discussed.

## Fe

On the basis of bulk crystal studies, Fe is considered to be more reactive than Ni [16]. Clearly, it achieves an earlier onset of reactivity, as only the very smallest Fe particles catalyze nanotubes, in this case SWNTs. Therein, Fe might be expected to readily react with  $C_2H_2$ , particularly since it reacts with CO. One might even predict that CO, as a less reactive carbon source could yet play a similar role in restricting the rate of carbon supply through  $C_2H_2$  dissociative adsorption, as it does with Ni. The difference here is that it would also contribute to the carbon supply.

With CO replaced by a balance of He, the gas mixture containing  $C_2H_2$ , as the only carbon source, was tested using Fe. No SWNTs were catalyzed. Only metal catalyst particles were observed. Using the CO/ $C_2H_2$  gas mixture, no definitive increase in SWNT yield was observed. While there may be some synergism between these reactant gases, the absence of an increase in SWNT yield suggests that any synergism is marginal at best. These results demonstrate the selective reactivity of Fe towards CO.

Notably, in either the CO or CO/ $C_2H_2$  gas mixture, Fe does not catalyze MWNTs or nanofibers. Catalysis of either would require larger Fe particles, which are generally not observed in our flame system. If the larger particles that are present were active towards MWNT or nanofiber synthesis, then these products would be expected, given similar temperature and residence time scales to those for Ni. Instead only the smallest Fe nanoparticles, roughly 1 nm in size are catalytically active. They exclusively catalyze SWNTs. The absence of MWNTs or nanofibers despite the presence of suitably sized particles suggests a decline in reactivity with increasing particle size, in contrast to Ni.

## Metal Nanoparticles

In a metal nanoparticle, the density of electronic states is finite and the traditional conduction and valence bands are absent due to the small number of constituent atoms [17]. With  $> 75\%$  of the atoms residing at the surface for a 1 nm particle, the particle properties will largely be determined by the surface atoms. This will be particularly true for those atomic orbitals not participating (contributing electron density) in the free conduction band of the metal, such as the 3d orbitals of the transition metals [16]. If the electronic properties of a metal nanoparticle resembles those of the individual element, given the finite size and high surface area, then based on energetics associated with its outer electron configuration,  $[Ar]5s^23d^6$ , Fe atoms can achieve a stable half filled d-shell by loss of electron density. Such is the case with donation of electron density to an adsorbate, e.g. CO, which undergoes dissociation primarily by accepting electron density from the catalyst metal. In contrast, acceptance of electron density (by the Fe nanoparticle) might be expected to be energetically unfavorable, given the increase in energy associated with pairing electron density within the d-shell orbitals. Therein, Fe would be expected to be unreactive towards  $C_2H_2$ , which undergoes dissociation primarily by donating electron density to the catalyst metal.

The situation for Ni is exactly opposite. Adopting the premise that the individual elemental identity still governs the electronic properties of the surface atoms and hence, their reactivities, it would be energetically favorable for Ni to accept electron density to achieve a more stable, filled d-shell, namely  $[Ar]5s^23d^{10}$ . Therein, Ni would be expected to be highly reactive towards adsorbates which donate electron density, e.g.  $C_2H_2$ . Correspondingly, Ni would be unreactive towards adsorbates that accepted (withdrew) electron density from the metal nanoparticle, e.g. CO.

Admittedly, the size dependent reactivities and selective reactivities towards the different reactive gases required additional study. Undoubtedly, other factors are also integral to these results. Some possibilities include thermal restructuring, adsorbate-enhanced restructuring and electronic interactions between adsorbates mediated by the catalyst particle. Our previous studies have discussed these effects in other synthetic systems [10, 14]. Further work remains to assess their relative contributions to CNT synthesis within the flame environment.

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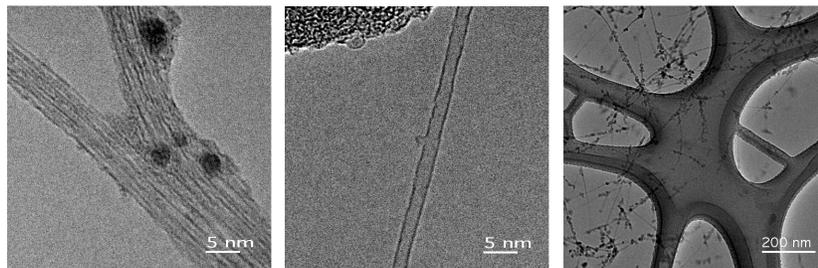


Figure 1. Representative TEM images of Fe-catalyzed SWNTs using a CO gas mixture. Both individual and bundled SWNTs were produced, though bundles were much more prevalent.

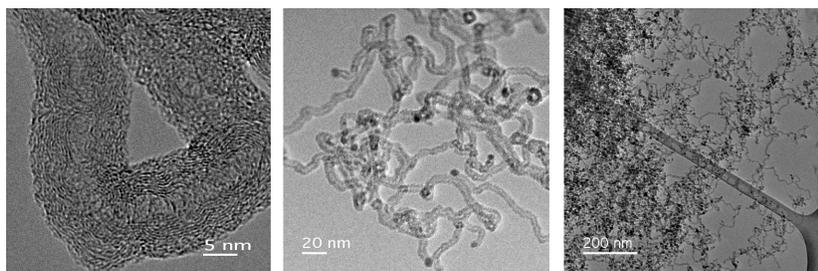


Figure 2. Representative TEM images of Ni-catalyzed nanofibers using a CO/C<sub>2</sub> gas mixture. Catalyst particles are evident at the tips of the nanofibers where exposed in (b). Image c) illustrates the undulation of the graphene segments comprising the nanofiber.